Principal component analysis for kinetic scheme proposal in the thermal pyrolysis of waste HDPE plastics

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Roberto Aguado *, Gorka Elordi, Aritz Arrizabalaga, Maite Artetxe, Javier Bilbao, M. Olazar

Department of Chemical Engineering, University of the Basque Country, PO Box 644, E48080 Bilbao, Spain

HIGHLIGHTS

- Formation rates of polyolefins thermal pyrolysis products are analyzed by PCA.
- PCA allows discriminating grouping by molecular size or bond nature.
- Grouping by molecular sizes is helpful for the proposal of kinetic schemes.
- A scheme based on the formation of waxes as intermediates is proposed.
- These intermediates crack to form gas (C_1–C_4), liquid (C_5–C_{11}), and aromatics.

ARTICLE INFO

ABSTRACT

Principal Component Analysis (PCA) has been used to process the data obtained from the batch pyrolysis of high density polyethylene (HDPE) in order to recognize trends in the formation rates of the large number of components in the product stream. Two different criteria for component grouping have been compared, i.e., according to molecular size, and the nature of C—C bond. The choice of the suitable criterion is crucial in order to establish the kinetic scheme, and PCA has proven to be a very helpful tool. The multivariate analysis applied to the lumps obtained according to the molecular size of the components provides very useful information, which allows proposing similar kinetic schemes to those in the literature, but with significant details involved in the definition of the lumps and their distribution between primary and secondary reactions. Furthermore, although there are substantial differences in the formation rate of single-ring aromatics (which are particularly affected by temperature), PCA carried out by grouping the products according to the nature of their C—C bond does not provide relevant information concerning differences in the performance of the main products (aliphatic hydrocarbons).

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1. Introduction

According to 2013 Annual Report of the European Association of Plastics Manufacturers [1] plastic production in 2012 amounted to 57 M tonnes in Europe and 288 M tonnes worldwide. Thanks to a growing public awareness and the consequent improvements in plastic waste management policies, landfill has decreased in EU-27 over the last 5 years. In fact, the recovered fraction is now higher than the amount sent to disposal/landfill sites since 2008. Recycling (both mechanical and chemical) is the preferred option for waste plastic, as the product shelf life is increased. Nevertheless, less than 25% of the 25.1 M tonnes of waste plastic generated in Europe in 2011 was suitable for recycling, which is due to the production of composites and specially designed plastics, the use

of new methods that improve the mechanical and superficial properties of the plastics, and the high cost of separation processes. The rest of the recovered fraction is intended for energy recovery (14.9 M tonnes recovered, i.e., 59% of waste plastic).

The polyolefins (HDPE, LDPE, LLDPE, PP) and the polyaromatics (PS, EPS) account for more than 55% of the European plastic production. Although they have similar physical and chemical properties and their individual separation is complicated and cost intensive, this fraction could be easily isolated from other MSW/plastic fractions using commercially available density-based separation methods [2]. Although this fraction would not be valid for mechanical recycling owing to its composition, properties, and thermal behavior, it can be upgraded by chemical recycling. Thermochemical methods would allow the (re)generation of hydrocarbon feedstock, and therefore mitigate crude demand and fill in the gap between waste-to-energy and mechanical recycling [3,4]. Pyrolysis is an attractive option to obtain hydrocarbons from

plastic wastes, as has been reported in the literature. Aromatic yields above 60 wt% have been obtained in the pyrolysis of polystyrene [5,6] and rejected streams of packaging plastic wastes from sorting plants [7]; more than 55 wt% of light olefins in the catalytic pyrolysis of HDPE [8–10]; and yields of gasoline above 55 wt% in the pyrolysis of HDPE with a spent FCC catalyst [11]. HDPE has been chosen in many of these studies as a plastic waste sample, because the behavior of the rest of the polyolefins (LDPE, LLDPE, ULDPE, PP) is similar [12–14].

These results illustrate the potential pyrolysis has to become the plastics chemical recycling (tertiary) technology par excellence and allow for optimism in the search for solutions to the pressing problem involving the management of this waste. However, scaling-up the pyrolysis reactor from lab to industrial size is not easy, since there is an insufficient understanding of the underlying reaction pathways, thereby preventing a quantitative prediction of the full product distribution [15]. In fact, although there are many kinetic studies regarding the pyrolysis and catalytic pyrolysis of polyolefins, most of them have been carried out in thermogravimetric analyzers [10,13,16–21] with minor samples and small particles; or with devices that do not operate under conditions equivalent to those of industrial units [22,23]; that is, they do not operate under ultrafast heating and continuous plastic waste feed and product stream. To sum up, the results of these studies should be taken with caution for their application in industrial processes [18]. Kinetic knowledge is essential for the determination of the optimum conditions for maximizing a given product [24] and for the design and simulation of commercial reactors [25]. Thus, kinetic studies are especially relevant when they have been carried out in reactors designed to overcome the current limitations for scaling up industrial ovens [26–28]. These reactors should have the same configuration as commercial designs, and product formation should be modeled according to kinetic schemes that adequately predict the result of the complex reactions occurring in the thermal degradation of the large molecular chains of the polymers.

Regarding the kinetic schemes for polyolefin pyrolysis, Westerhout et al. [29] proposed a pioneering model in which the primary devolatilization reaction yields mainly intermediate wax-like products that are cracked to smaller hydrocarbons following secondary reactions. These authors stated that low molecular weight alkanes and alkenes are thermodynamically unstable at high temperatures, being converted into aromatic compounds (tertiary reactions) and, in the case of sufficiently high residence times, coke could be formed. In a subsequent work, Elordi et al. [30] observed that this model does not effectively predict the results obtained in a conical spouted bed reactor in the 450–715 °C range. This disparity between the aforementioned models could be related to the lower amount of secondary and tertiary reactions that take place in this type of reactor due to the very short residence times attained. These authors tested up to eight new kinetic schemes. The best fit was achieved with a model in which polyethylene degrades to give gas, liquid, and wax; with the latter undergoing secondary reactions to give liquid and aromatics, which in turn and at high temperatures, produces more char. In a more recent work, Huang et al. [28] proposed a mechanistic scheme including the main features and kinetic reaction schemes for polymer degradation over cracking catalysts, and discussed the role of the carbenium ion in catalytic cracking chemistry. This proposal does not group the components as determined by their molecular size or state at ambient temperature (gas, liquid, wax), but puts forward another criterion based on the nature of the chemical bonds that are characteristic of the different molecules. Hence, products are lumped into paraffins, olefins, and aromatics.

Selecting the grouping criterion that best represents the multiple cracking reactions the polymer undergoes is a key factor for the proposal and validation of a kinetic scheme. Accordingly, analysis tools are required to objectively and quantitatively elucidate the benefits of one criterion over another. In this paper, Principle Component Analysis (PCA) is proposed in order to select the best criterion for lumping the reaction products, given that this mathematic technique of multivariate analysis is suitable for recognizing patterns in complex problems [31–34], and its potential has been proven in the kinetic study of waste material pyrolysis [35].

2. Experimental

Pyrolysis experiments have been carried out in the 550–650 °C range in a conical spouted bed reactor described elsewhere [36,37]. The raw material is HDPE manufactured by Dow Chemical (Tarragona, Spain), with its main properties being as follows: average particle size: 4 mm; molecular weight (M_w): 46,200 g/mol; polydispersity: 2.89; density: 940 kg/m^3; and higher heating value: 46,230 kJ/kg.

Runs have been carried out in batch mode. The reactor bed consists of 30 g of sand (particle size between 0.63 and 1 mm). In all cases the fluidizing agent was N_2, with a velocity of 1.2 times of that corresponding to the minimum spouting regime. 1 g of HDPE is fed into the reactor, and during each run, gas samples have been taken from the product stream at given reaction times, in order to carry out on-line monitoring by gas chromatography. This analysis method allows monitoring the evolution over time of all the volatile products with a molecular size smaller than 20 carbon atoms. The remainder of products correspond to heavy fractions, including light waxes, with boiling points between 343 °C and 525 °C, and heavy waxes, with higher molecular weights and boiling temperatures [38]. In view of their size, the characterization of waxes requires more specific analytical techniques (GPC/SEC, FTIR, distillation) that could not be settled as on-line analysis techniques, and therefore are not suitable for on-line monitoring. However, use of internal standards in the experiments allowed mass balance closure with an accuracy of close to 98%, with the yield of waxes being determined by difference.

A tool has been developed in Scilab for the multivariate analysis of the experimental results. The program developed uses the *pca* function to determine the correlation circle and the scree plot, and the *fminsearch* optimization function for the orthogonal rotation (varimax rotation), with the aim being to facilitate the interpretation of the results.

3. Results and discussion

3.1. Experimental results

The conversion is usually defined in waste pyrolysis as follows [39,40]:

$$X_n = \frac{W_o - W}{W_o - W_\infty} \tag{1}$$

where W, W_o and W_∞ are the masses at time t, at the beginning and at the end of the reaction. Given that under the experimental conditions for pyrolysis in the spouted bed reactor, e.g., short residence time and high N_2 dilution, no solid product is formed in polyolefin and polyaromatic pyrolysis, thereby Eq. (1) simplifies to:

$$X_n = \frac{W_o - W}{W_o} \tag{2}$$

According to this definition, the yield of each product or lump (X_i) is defined as:

$$X_i = \frac{W_i}{W_o} \tag{3}$$

where W_i is the mass of product or lump i at a given time. The yields of the individual products and lumps obtained in the thermal pyrolysis of HDPE in the temperature range studied in this paper have been published in a previous one [41].

The latter is the definition of yield used in the multivariate study, but it is not suitable for building typical X_i vs. T graphs. The standard scale masks trends and similar performances of the lumps, because the final yield that each lump reaches is very different. Accordingly, a new parameter called modified yield, X_i^*, has been defined and determined as follows:

$$X_i^* = \frac{X_i}{X_i^\infty} = \frac{W_i}{W_i^\infty} \tag{4}$$

where X_i^∞ and W_i^∞ are the yield and mass of the component or lump i at the end of the reaction, respectively. Fig. 1 shows the results obtained in the thermal pyrolysis carried out in batch mode at 550 °C, 600 °C, and 650 °C. Products have been grouped according to their molecular size in the following: CH_4, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}–C_{20} and aromatics. The aromatics have been split because the original structure of the polymer does not have any aromatic rings, so they are unlikely to have been formed as a consequence of a main chain sigma bond cleavage reaction, but rather as a result of condensation secondary reactions [29], and they are coke precursors at high temperatures [42]. A continuous line in Fig. 1 shows the average evolution of the volatile products
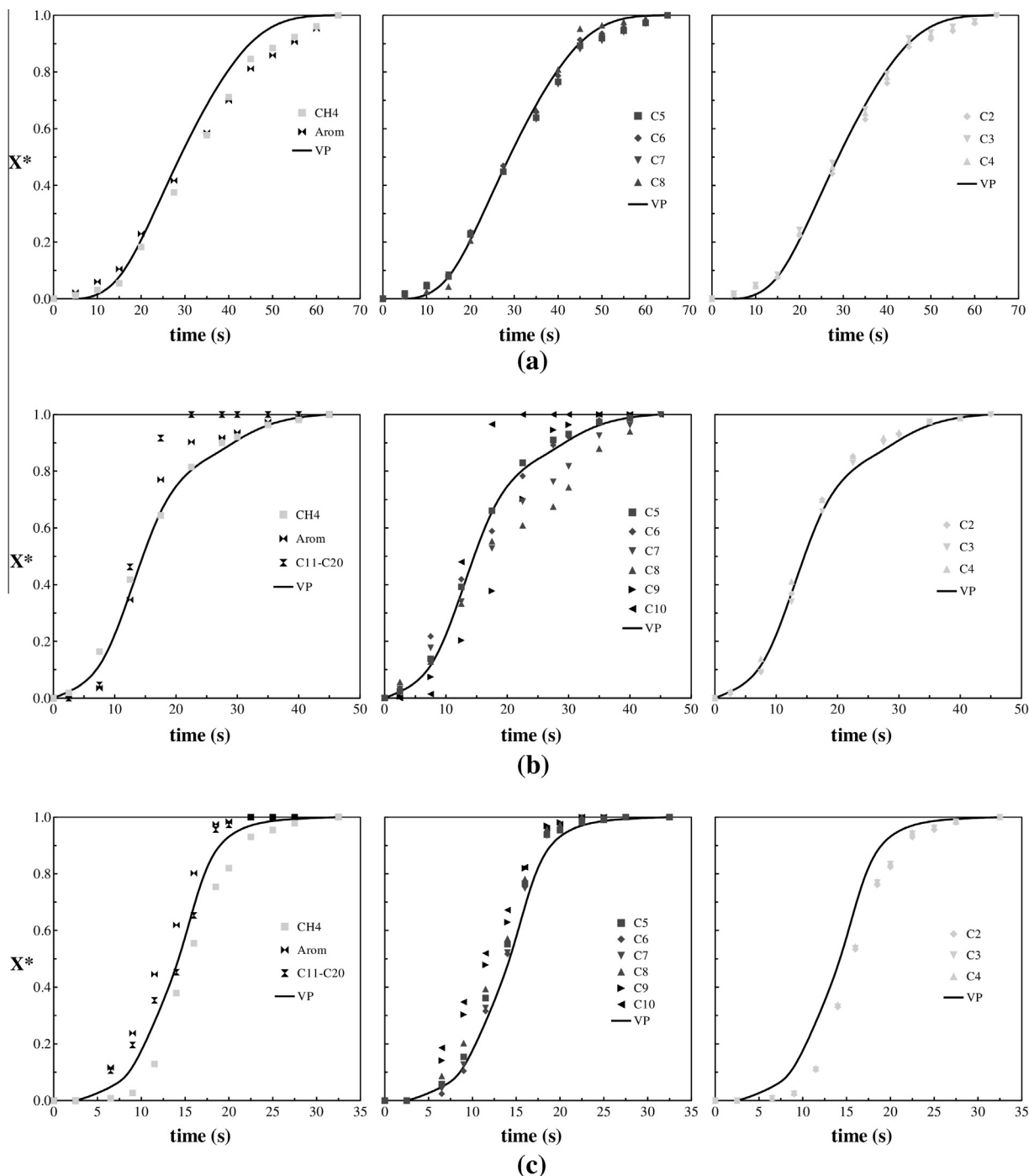
Fig. 1. Evolution with time of the modified yield of the different lumps grouped according to their molecular size in the batch thermal pyrolysis, (a) 550 °C, (b) 600 °C, (c) 650 °C.

(VP), corresponding to the sum of all the product families quantified by gas chromatography.

At 550 °C (Fig. 1a) methane and the aromatics have a similar trend, with a slightly slower evolution than the non-aromatic $C_5–C_{11}$ hydrocarbons and the rest of the C_{4-} gas components, which account for 26 wt.% of all the volatile products (VP) formed. The C_{4-} gas components follow a similar trend to the non-aromatic $C_5–C_{11}$ hydrocarbons, which account for almost 70 wt.% of the VP at this temperature. A wider dispersion is observed at 600 °C (Fig. 1b), although gas components, 28 wt.% of the VP, again follow a similar trend (including methane in the gas components). However, remarkable differences are observed in the components that constitute the gasoline lump (60 wt.% VP). C_5 and C_6 components undergo a similar formation rate to the gas components and most of the VP, but C_7 and C_8 hydrocarbons evolve more slowly, and heavier products (C_{10} and $C_{11}–C_{20}$) are formed much faster, reaching their maximum yield at relatively short reaction times. The experiments carried out at the highest temperature studied, 650 °C (Fig. 1c), clearly show the effect of temperature on the reaction kinetics, as the time needed for the original polymer to fully degrade becomes half of that required at the lowest temperature studied. A similar formation rate of the gas components (C_{4-}) is observed again, as was the case at the lower temperatures studied. These gas components constitute almost 40 wt.% of the VP at this temperature. The formation rate of these components is slightly slower than those of liquid components. Among the liquid components, those in the $C_5–C_8$ range record a similar trend, whereas the heaviest ones, C_9 and C_{10}, are formed faster. These results are the basis for proposing models in which waxes are formed as primary products from the direct cracking of long polymer chains, and they subsequently undergo gas phase secondary cracking reactions to form other fractions [29,30].

Fig. 2 shows the results of the same experiments (HDPE thermal pyrolysis at 550 °C, 600 °C, and 650 °C), although in this case the product components have been grouped according to the nature of their C—C bonds. Thus, products have been grouped as follows: light alkanes (LA), light olefins (LO), paraffins (P), isoparaffins (iP), olefins (O), benzene (B), toluene (To), ethylbenzene + xylenes (EthylBz + Xyl), C_9 aromatics (C_9 Arom), C_{10} aromatics (C_{10} Arom), C_{11} aromatics (C_{11} Arom), and naphthenes. As in Fig. 1, the average evolution of the VP is shown as reference.

Fig. 2a data (corresponding to 550 °C) show that light olefins follow a similar trend to the VP as a whole. Light alkanes and toluene show a slower formation rate, as observed for methane in Fig. 1a. Nevertheless, all the other aromatics detected at this temperature (benzene, ethylbenzene, and xylenes) and the other product families (paraffins, isoparaffins, olefins, and naphthenes) have a similar formation rate throughout the reaction. Taking into account the properties of the polymer in the feed (a polyolefin), the prevailing products are components with double bonds. Therefore, light olefins (C_{4-}) and olefins ($C_5–C_{11}$) account for more than 50 wt.% of the VP. The delay for toluene (the most common aromatic at this temperature, 3.2 wt.%, is much higher than the sum of the remaining aromatic components) and light alkanes confirms that aromatic rings are formed as a consequence of condensation secondary reactions [43].

Fig. 2b corresponds to the results of the experiments carried out at 600 °C. Similarly to the experiments at 550 °C, toluene and the remaining aromatic components have a slower formation rate at 600 °C. The aromatic components account for less than 10 wt.% of the VP at this temperature, with olefins being the main components, 40 wt.% of the VP. The yield of isoparaffins increases in a more pronounced way than at 550 °C, reaching 35 wt.% of the VP. Although the results obtained at 650 °C are not as disperse as those obtained at 600 °C, they confirm the trends observed at lower temperatures.

3.2. PCA results

Figs. 1 and 2 give clues about the common trends of some of the components and validate the hypothesis of this work concerning the significance of having criteria to group products for the proposal of kinetic schemes and even for classifying the products as primary or secondary in order to progress in the proposal of mechanisms (cleavage, condensation) for transforming some products into others. Nevertheless, the information obtained from those figures is somewhat qualitative, and therefore lacking rigor. Moreover, information is lost in these types of representations due to the dense cloud of experimental points that prevents detecting the time when maximum production is achieved (corresponding to the maximum in the dX_*/dt curve). Multivariate analysis techniques like PCA are then planned for a systematic analysis of the trends of each lump. The fact that all the products, whether they are primary or secondary, are formed from the raw polymer has to be taken into account when this statistical technique, PCA, is applied to the study of pyrolysis, because all the products are related to each other, as observed in the correlation matrix.

Another peculiarity of the application of PCA to the batch pyrolysis process, which has already been observed in a previous paper, is that a single component accounts for more than 95% of the total variance (Table 1). Accordingly, the points are vertically aligned in the correlation circle before the varimax rotation is applied.

The results of the eigenvalue matrix (Table 1) confirm that the employment of only two components suffices to explain the total variance. Thus, the correlation circle can be elaborated and the varimax rotation applied with the corresponding 2D representation for the analysis of the experimental results. Fig. 3 shows the loadings of the 12 lumps (variables), in which the products of the thermal pyrolysis of HDPE at 550 °C, 600 °C, and 650 °C have been grouped according to their molecular size (carbon atom numbers).

The results shown in Fig. 3a, corresponding to the batch thermal pyrolysis of HDPE at 550 °C arranged by their molecular size, confirm and complement the trends observed in Fig. 1a. Four groups or lumps may be distinguished. The first one, as pointed out in the X_* vs. t plot, consists of CH_4 and the aromatics, and is related to component 2. A second group is made up of C_2, C_5, and C_7 components; a third one is made up of C_3, C_4, and C_6, (they stand over the horizontal axis in Fig. 3a and are not related to component 2); and a fourth one made up of only C_8. As observed, C_8 products are clearly related to component 1 and their behavior is very different to those products that are solely related to component 2, i.e., aromatics and methane. The ability of PCA to find analogous performances is noteworthy. Thus, although in Fig. 1a the performance of aromatics and methane is visibly different to the remaining products, the multivariate analysis allows discerning slight differences among the gases, as C_2 (mainly ethylene) is separated from C_3 and C_4 (mostly propylene and butenes), and even detecting certain differences in the liquid fraction, where C_5 and C_7 products, mostly olefins, have a slightly different trend compared to C_6 and C_8 products, with a higher concentration of isoparaffins. This information is very helpful for the proposal of new kinetic schemes.

The correlation circle after the varimax rotation for the results carried out at 600 °C in batch mode (Fig. 3b) shows that, as in Fig. 1b, the performance of $C_1–C_6$ components is quite similar, but different to that of $C_7–C_9$ products. C_{10} and C_{11+} are the sole products that appear in the second quadrant, and significantly affected by component 2. These results are explained by the much faster formation of C_{10} and especially C_{11+} products.

The results obtained at 650 °C when arranging the products according to their molecular size (Fig. 3c) confirm some of the groups already proposed and establish new ones. All these results allow proposing the lumps that should be considered in the kinetic scheme and establishing the sequence in which the reactions take
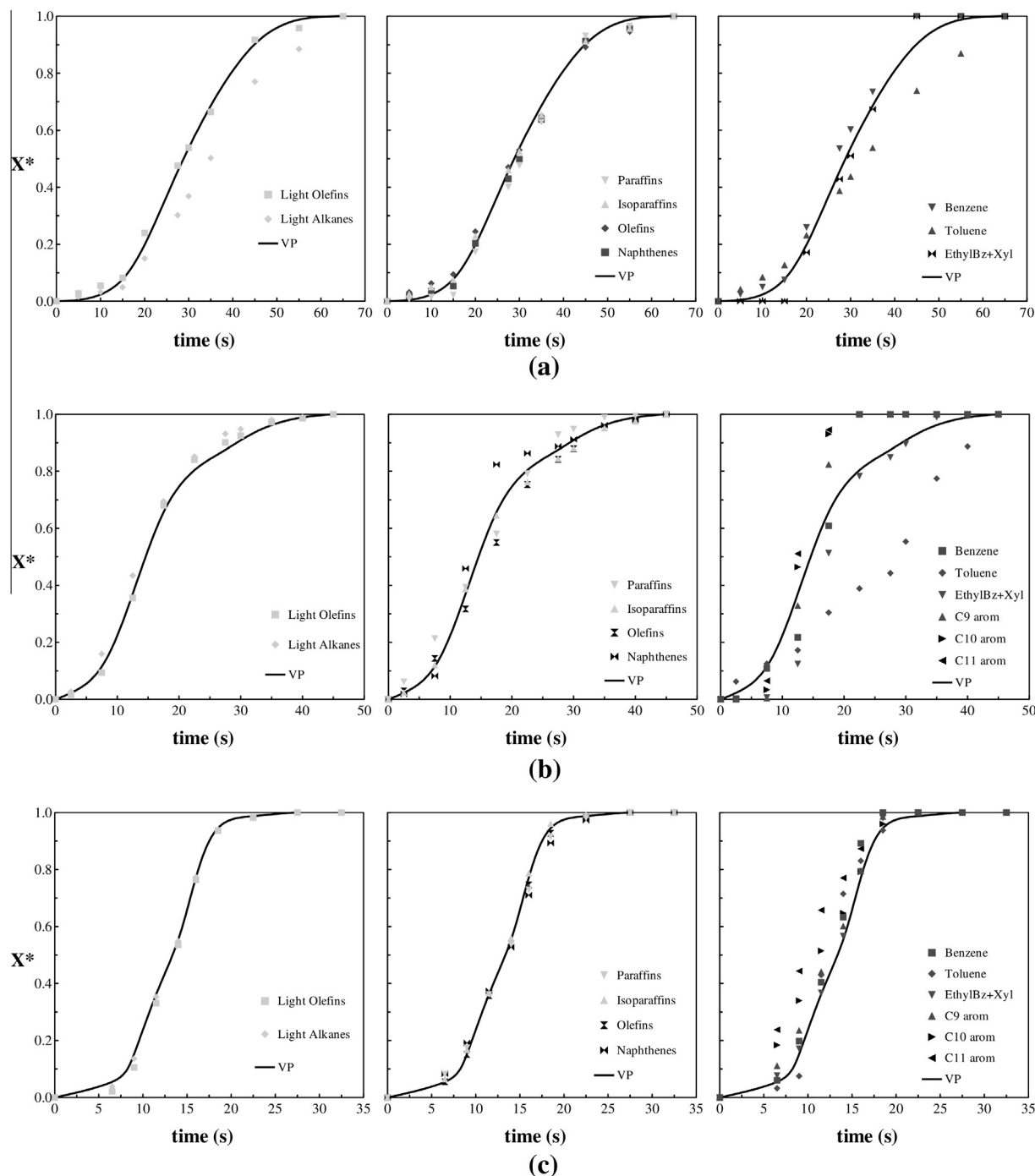
Fig. 2. Evolution with time of the modified yield of the different lumps grouped according to the nature of their C—C bond in batch thermal pyrolysis, (a) 550 °C, (b) 600 °C, (c) 650 °C.

place. Gases have a visibly different performance, as they are all in the third quadrant and negatively related to component 2, whereas the light liquid fraction (C_5–C_8) follows a different trend. The performance of aromatic components, which varies with temperature, suggests they are secondary products that are favoured by an increase in temperature. Other components are also affected by secondary reactions, because they are grouped in a different way when temperature is increased.

Westerhout et al. [29] proposed that waxes were the only primary product, but this statement has been subsequently questioned by other authors [30,42], who also proposed gases and liquid as primary products. The results obtained at 550 °C and

600 °C show that C_{10-} products have a different performance to the heavier hydrocarbons, i.e. the latter are formed sooner. Thus, as Gonzalez et al. [44] proposed, products heavier than the gasoline fraction, C_{11+}, should be considered as waxes (or pyrolysis solid products) in the thermal pyrolysis of polyolefins due to their similar formation rate. As temperature is increased, the cracking of the polymer is more severe and at 650 °C even the lighter fraction of waxes, C_{11}–C_{20}, undergoes secondary cracking reactions to give light hydrocarbons, C_{10-} [41]. Furthermore, the location of methane together with the aromatic components at 550 °C, close to the gas products at 600 °C, and the different trend the gases follow at 650 °C are indications that the gas lump comes from the severe

Table 1
PCA initial statistics matrix.

| Component	Initial eigenvalues		
	Total	Variance (%)	Cumulative (%)
550 °C, molecular size			
1	8.987	99.85	99.85
2	0.012	0.13	99.98
600 °C, molecular size			
1	11.746	97.88	97.88
2	0.204	1.70	99.58
650 °C, molecular size			
1	11.844	98.70	98.70
2	0.146	1.22	99.92
550 °C, bond type			
1	8.939	99.32	99.32
2	0.054	0.60	99.92
600 °C, bond type			
1	11.555	96.29	96.29
2	0.359	2.99	99.28
650 °C, bond type			
1	11.926	99.38	99.38
2	0.057	0.47	99.86

cracking of the different products that make up the wax fraction. These cracking reactions yield intermediate products (olefins) that follow cyclization, aromatization reactions, producing aromatics and light alkanes.

These results evidence that the kinetic scheme for HDPE thermal pyrolysis at the 550–650 °C temperature range should take into account at least 5 lumps: (i) the primary products derived from the raw polymer cracking, which are generally referred to as waxes; (ii) gaseous products, C_1–C_4, which are primary or secondary products depending on the reaction; (iii) non-aromatic C_5–C_9 hydrocarbons, which are primary or secondary products; (iv) aromatic products (clearly secondary products); (v) the char, which is a tertiary product derived from polyaromatic products [45], although it has not been detected in this study because we operated at temperatures lower than 700 °C and with relatively low residence times for the pyrolysis products. As a conclusion, Fig. 4 shows the kinetic scheme for HDPE thermal pyrolysis. The continuous arrows are primary reactions, whereas the dashed ones are secondary and tertiary ones.

This scheme is similar to the one proposed by [29], with the inclusion of a new lump (the non-aromatic C_5–C_9 liquid fraction), given that the formation rate of these components cannot be explained by any of the other lumps. Besides, the scheme does not consider the formation of aromatics from gases because there is no evidence of this formation in the multivariate analysis, i.e., they are not related by component 1 or 2 in the PCA, and so an increase in one lump does not imply a decrease in the other.

In order to decide whether the criterion of grouping according to molecular size or the nature of the C—C bonds is the more suitable, Fig. 5 shows the results of the same experiments, but grouping the products into the following categories: light alkanes (LA), light olefins (LO), C_5–C_{11} paraffins (P), C_5–C_{11} isoparaffins (iP), C_5–C_{11} olefins (O), benzene (B), toluene (To), and ethylbenzene + xylenes (EthylBz + Xyl), C_9 aromatics (C_9 Arom), C_{10} aromatics (C_{10} Arom), C_{11} aromatics (C_{11} Arom), and naphthenes.

The results corresponding to the lowest temperature studied (550 °C, Fig. 5a) evidence a similar performance for most of the main products in thermal HDPE pyrolysis; that is, aliphatic hydrocarbons, except light alkanes, have a similar formation rate. Light alkanes, as well as toluene, are located in the second quadrant, being positively affected by component 2. This trend has already been observed in Fig. 3a for aromatics and methane. Nevertheless, single-ring
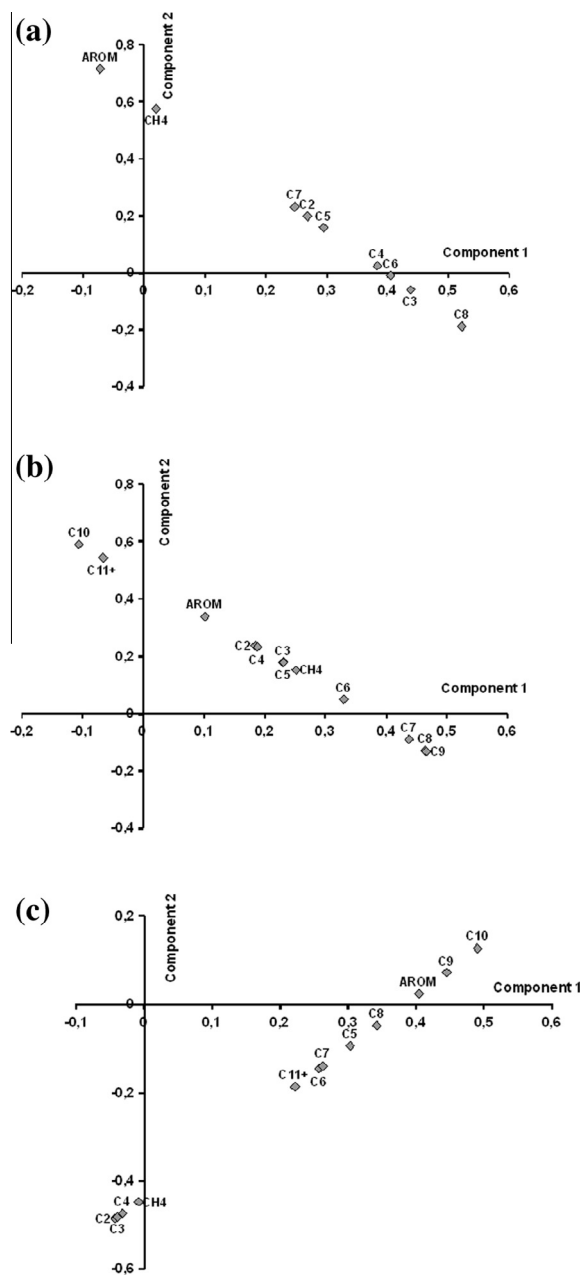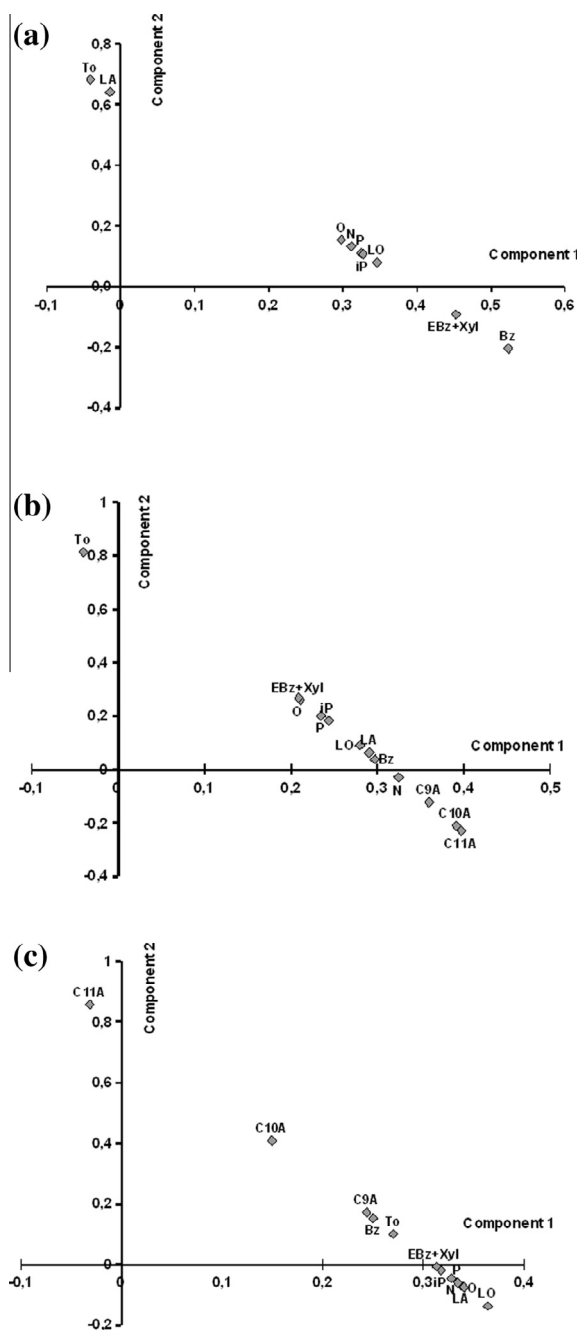

Fig. 3. Loadings of the 12 lumps (variables) grouped according to the molecular size in the batch thermal pyrolysis of HDPE, (a) 550 °C, (b) 600 °C, (c) 650 °C.
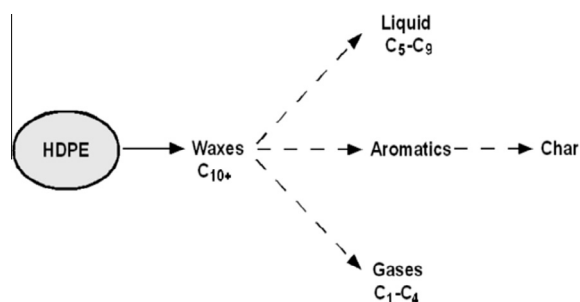
Fig. 4. Kinetic scheme proposed for the thermal pyrolysis of HDPE.

aromatics and light alkanes are minor products, as they account for less than 5 wt.% of the product yield at the temperature studied. Furthermore, the rest of the aromatics identified at this temperature

Fig. 5. Loadings of the 12 lumps (variables) grouped according to the nature of their C—C bond in the batch thermal pyrolysis of HDPE, (a) 550 °C, (b) 600 °C, (c) 650 °C.

(benzene, ethylbenzene, and xylenes) record a different formation rate compared to that of toluene. The difference between toluene and the rest of the aromatics remains at 600 °C (Fig. 5b), although an increase in temperature induces notable alterations in the grouping into lumps. Light alkanes record a similar formation rate to all the other aliphatic acyclic hydrocarbons or to the lightest aromatic components (benzene, ethylbenzene, and xylenes). Furthermore, the remainder of the aromatic components and acyclic hydrocarbons (C_9–C_{11} aromatics, and naphthenes) are located in the fourth quadrant, being closely related to component 1.

Finally, the correlation circle of the results obtained at 650 °C when the components are arranged according to the nature of their C—C bonds (Fig. 5c) corroborates that the formation rate of all the acyclic aliphatic hydrocarbons is similar. Moreover, the main

differences are observed for the aromatic components. Thus, the lighter ones (benzene, toluene, xylenes, ethylbenzene, and C_9 aromatics) appear grouped in the graph, but C_{10} and C_{11} are substantially separated from the remaining pyrolysis products.

Given that the yield of single-ring aromatics accounts for less than 3 wt.% of the product stream, the yield of acyclic aliphatic components, particularly isoparaffins and olefins [41], is over 95 wt.% and the information obtained from PCA by grouping the product components according to the nature of the C—C bond has not provided any relevant information concerning different performances between isoparaffins and olefins. Therefore, kinetic scheme proposals should be based on the lumps defined according to molecular size [23,29,30,43] and not on the nature of the C—C bond [28].

4. Conclusions

PCA has proven to be a versatile method for verifying the criteria used to group the large number of product components that are formed in the thermal pyrolysis of polyolefins. In fact, PCA allows the detection and recognition of similar performance patterns among different compounds or lumps, and therefore helps to establish a precise definition of lumps and the hierarchy of the reactions, differentiating between primary and secondary products.

The grouping of the HDPE thermal pyrolysis products, in the 550–650 °C range, according to their molecular size, allows a precise definition of the components within the most common lumps used in the literature: gas (C_1–C_4), liquids (non-aromatic C_5–C_{11}), aromatics, and waxes (C_{11+}). Moreover, multivariate analysis shows that waxes are the intermediate compounds, and the remaining lumps are produced in secondary reactions from these waxes and the condensation of derived products.

The grouping of products according to bond type shows that condensation, cyclization and aromatization producing single-ring aromatics are clearly affected by temperature. Nevertheless, multivariate analysis applied to major pyrolysis products (acyclic aliphatic products, especially olefins and isoparaffins) does not allow extracting conclusive information for the proposal of kinetic schemes based on the grouping of compounds according to hydrocarbon families.

Acknowledgements

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